

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

N-Nitrosodiphenylamine is used as a vulcanization retardant in rubber compounds used to make tires. There is some evidence to suggest it is produced by microorganisms in the environment. In 1988 it was being produced and used by two manufacturers in the United States (TRIM 1990). Currently, only one manufacturer in the United States produces and uses *N*-nitrosodiphenylamine (SRI 1090). Releases to the environment occur from effluent discharges generated from its production and use and from leachate at hazardous waste sites.

N-Nitrosodiphenylamine exists in the vapor phase in the atmosphere. It is subject to volatilization from water. Significant leaching is not expected to occur because of its low soil mobility. In the aquatic environment, *N*-nitrosodiphenylamine partitions from the water column to sediments and suspended particulate organic matter. It is subject to photolysis and biodegradation. Biomagnification in the aquatic food chain is not considered to be a major environmental fate process since *N*-nitrosodiphenylamine has a low potential for bioaccumulation in aquatic organisms.

The general population of the United States does not appear to be exposed to any background levels of *N*-nitrosodiphenylamine. However, no studies investigating the concentrations of *N*-nitrosodiphenylamine in drinking water, foods, or ambient air were located.

N-Nitrosodiphenylamine has been identified in 172 of the 1,300 NPL hazardous waste sites (HAZDAT 1992). The frequency of these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

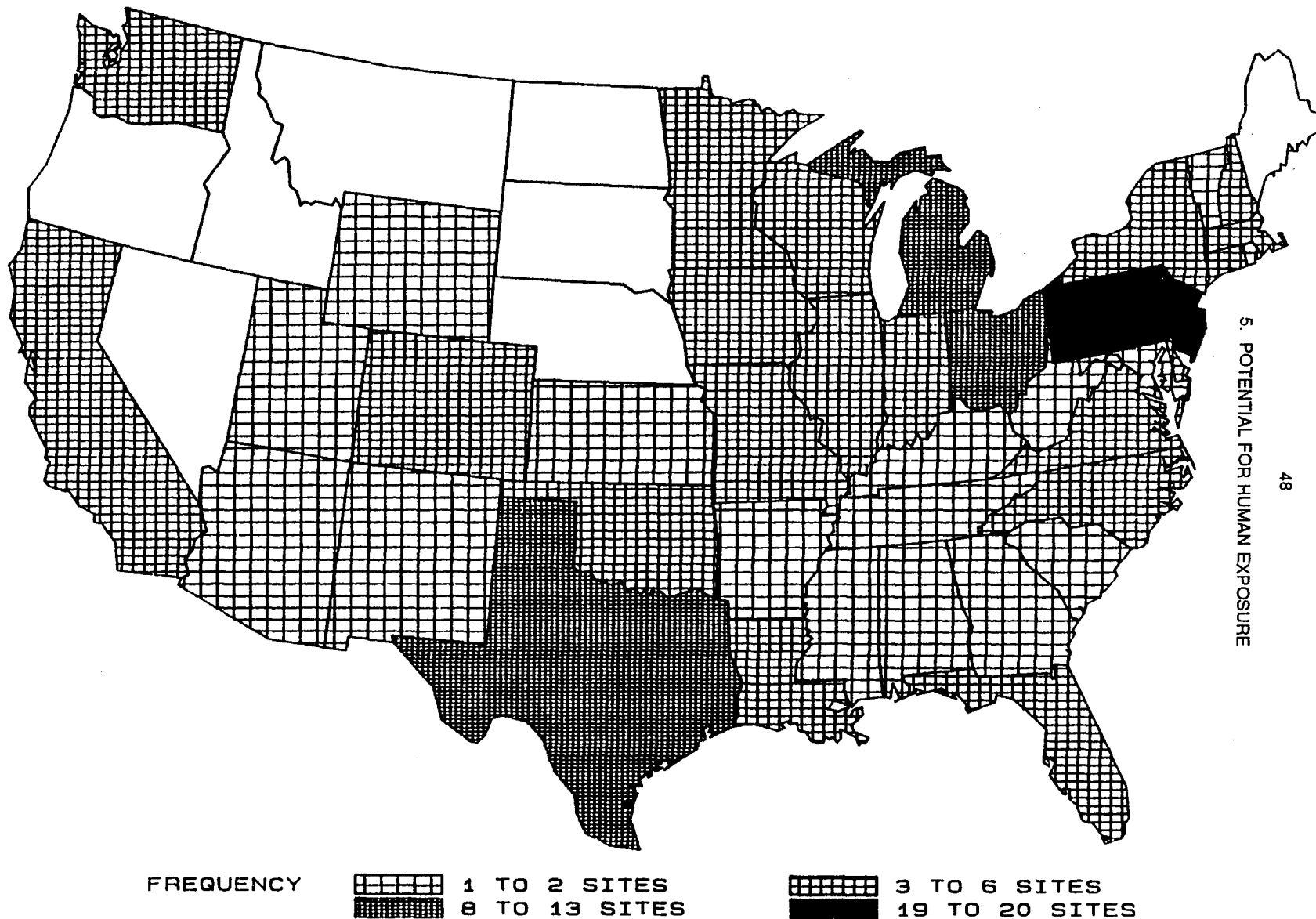
5.2.1 Air

N-Nitrosodiphenylamine may be released to the atmosphere from sewage sludge incinerators (Gerstle 1988) or from hazardous waste sites. Release of *N*-nitrosodiphenylamine to the environment can occur from effluent discharges generated from its production and use.

5.2.2 Water

N-Nitrosodiphenylamine may be released in industrial waste water (Rhoades et al. 1980). There is also evidence suggesting that some microorganisms produce *N*-nitrosodiphenylamine from diphenylamine and nitrate or nitrite in the environment (Ayanaba and Alexander 1973). Although this has only been shown for pure cultures under laboratory conditions, it may be a natural source of *N*-nitrosodiphenylamine in the environment. *N*-Nitrosodiphenylamine was detected in an estimated 3.6% of the groundwater and 0.71% of the surface water samples analyzed at NPL sites included in EPA's Contract Laboratory Program (CLP). Estimated geometric mean concentrations of 7.8 ppb in groundwater and 9.4 ppb in surface water were reported in the positive samples (CLPSD 1989). Note that the information used from the CLP Statistical Database (CLPSD) includes data from NPL sites only. According to the Toxics Release Inventory (TRI), an estimated total of at least 27 pounds of *N*-nitrosodiphenylamine was released to water from manufacturing and processing facilities in the United States in 1988 (TRI88 1990). Table 5-1 lists the amounts released from these facilities. The data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

FIGURE 5-1. FREQUENCY OF NPL SITES WITH N-NITROSODIPHENYLAMINE CONTAMINATION *



*Derived from HAZDAT 1992

TABLE 5-1. Releases to the Environment from Facilities
That Manufacture or Process N-Nitrosodiphenylamine^a

Facility	Location ^b	Reported amounts released in pounds						
		Air	Underground injection	Water	Land	Total environment ^c	POTW transfer	Off-site waste transfer
Arkansas Eastman Co.	Batesville, AR	0	0	27	0	27	0	300
Uniroyal Chemical Co. Inc.	Geismar, LA	0	34,000	0	0	34,000	0	0
Totals		0	34,000	27	0	34027	0	300

^aDerived from TRI88 (1990)

^bPost office state abbreviations used

^cThe sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

POTW = publicly owned treatment works

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5.2.3 Soil

N-Nitrosodiphenylamine potentially can be released to soil from leachate at hazardous waste sites, underground injection wells, or off-site waste transfer (TRISS 1990). There is also evidence suggesting it might be produced by some microorganisms under certain environmental conditions (Ayanaba and Alexander 1973). However, *N*-nitrosodiphenylamine was not detected in soil samples at any of the NPL sites included in the CLPSD (CLPSD 1989).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

N-Nitrosodiphenylamine has a vapor pressure of 0.1 mmHg at 25°C (HSDB 1990). It should exist almost entirely in the vapor phase in the atmosphere (Eisenreich et al. 1981).

N-Nitrosodiphenylamine is soluble in water (40 mg/L) (EPA 1982a). The Henry's law constant for *N*-nitrosodiphenylamine (6.6×10^{-4} atm-m³/mol) (EPA 1982a) indicates that volatilization from water will be a slow but significant transport process (Lyman et al. 1982).

The soil sorption coefficient (K_{OC}) for *N*-nitrosodiphenylamine was estimated to range from 830 to 1,830 (Lyman et al. 1982). This K_{OC} range is indicative of low mobility in soil; therefore, significant leaching is not expected to occur in most types of soil (Swann et al. 1983). In the aquatic environment, substantial partitioning from the water column to sediment and suspended particulate organic matter may occur.

The logarithm of *N*-octanol/water partition coefficient ($\log K_{OW}$) is a useful preliminary indicator of potential bioaccumulation of a compound. The $\log K_{OW}$ for *N*-nitrosodiphenylamine was estimated to range from 2.57 to 3.13, indicating a low potential for bioaccumulation (Banerjee et al. 1980; Barrows et al. 1980). An experimental bioconcentration factor of 217 was determined for *N*-nitrosodiphenylamine based on a continuous 14-day exposure study of bluegill sunfish with a mean *N*-nitrosodiphenylamine water concentration of 9.21 ppb (Barrows et al. 1980). The half-life of *N*-nitrosodiphenylamine in the fish was found to be less than 1 day when the fish were placed in pollutant-free water after the exposure period. The relatively low experimental bioconcentration potential and short half-life of *N*-nitrosodiphenylamine indicate that biomagnification in the aquatic food chain is not a major environmental fate process (Barrows et al. 1980).

5.3.2 Transformation and Degradation

5.3.2.1 Air

N-Nitrosodiphenylamine absorbs sunlight, suggesting a potential for direct photolysis in a sunlit environment (EPA 1979). Irradiation experiments using a benzene solution of *N*-nitrosodiphenylamine have shown that *N*-nitrosodiphenylamine is photodecomposed at sunlight wavelengths (Sharma et al. 1986). The rate at which photolysis occurs was not determined. *N*-Nitrosodiphenylamine also reacts with hydroxyl radicals in the atmosphere. An estimated half-life for this reaction is 7 hours (HSDB 1990).

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5.3.2.2 Water

The major environmental fate process for *N*-nitrosodiphenylamine in water is biodegradation. A static culture flask-screening biodegradability test was performed using domestic waste water as the microbial inoculum and 5 and 10 ppm of *N*-nitrosodiphenylamine as the test compound (Tabak et al. 1981). At the end of 7 days, 87% degradation was achieved in the original culture dosed with 5 ppm, and 47% degradation was achieved in the original culture dosed with 10 ppm. After the second 7-day incubation period, 100% degradation was achieved in the first subculture dosed with 5 ppm, while 63% degradation was achieved in the first subculture dosed with 10 ppm. After the fourth 7-day incubation period, 98% degradation was achieved by the third subculture dosed with 20 ppm. These results showed that *N*-nitrosodiphenylamine was degradable, with rapid microbial adaptation at concentrations of 5 ppm and with more gradual microbial adaptation at concentrations of 10 ppm (Tabak et al. 1981). No studies were located regarding hydrolysis and oxidation of *N*-nitrosodiphenylamine.

5.3.2.3 Soil

Biodegradation is the major environmental fate process for *N*-nitrosodiphenylamine in soil. In laboratory tests using a sandy loam soil, 68% of added *N*-nitrosodiphenylamine was degraded after 30 days of incubation, but amending the soil with wheat straw (to increase microbial activity) resulted in complete disappearance of added *N*-nitrosodiphenylamine in 10 days (Mallik and Tesfai 1981).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

No data were located regarding the levels of *N*-nitrosodiphenylamine in air.

5.4.2 Water

No data were located regarding the levels of *N*-nitrosodiphenylamine in drinking water. Only one positive detection was found for ambient surface waters. *N*-Nitrosodiphenylamine was detected (no concentration reported) in the Cuyahoga River, which feeds Lake Erie (Great Lakes Water Quality Board 1983).

5.4.3 Soil

N-Nitrosodiphenylamine was measured at a concentration of 47 mg/kg (47,000 ppb) in a soil sample collected in 1978 near a manufacturing facility (NIOSH 1983). It has also been detected (no concentration reported) in the soil-sediment-water complex of the Love Canal near Niagara Falls, New York (Hauser and Bromberg 1982).

5.4.4 Other Environmental Media

No reports of *N*-nitrosodiphenylamine detection in food or other environmental media were found in the available literature.

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5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population does not appear to be exposed to any background levels of *N*-nitrosodiphenylamine. No data were located regarding levels of *N*-nitrosodiphenylamine in air, drinking water, or foods.

The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983 estimated that 1,093 workers employed at 137 plants were potentially exposed to *N*-nitrosodiphenylamine in the United States (NOES 1990). The NOES database does not contain information on the frequency, concentration, or duration of exposure to *N*-nitrosodiphenylamine. The survey provides only estimates of workers potentially exposed to chemicals in the workplace.

N-Nitrosodiphenylamine was detected in the workplace air of an Ohio tire chemical factory in the spring of 1978. The concentrations of *N*-nitrosodiphenylamine ranged from 0 to 47 $\mu\text{g}/\text{m}^3$ (0-6 ppb) (Fajen et al. 1979, 1980). A scraping from a staircase in the factory contained 15,000 ppm of *N*-nitrosodiphenylamine. Additional monitoring conducted in Ohio during the spring of 1978 found no detectable levels of *N*-nitrosodiphenylamine in the workplace air of an industrial rubber products factory, an aircraft tire factory, a synthetic rubber and latex factory, and three tire plants (Fajen et al. 1979, 1980).

Levels of *N*-nitrosodiphenylamine ranging from not detectable to 12.35 $\mu\text{g}/\text{m}^3$ (1.5 ppb) in workplace air samples were detected at a Kelly-Springfield tire plant in 1979 in the United States (NIOSH 1984). Levels ranging from below detectable limits (5 ng per sample) to 160 ng/m^3 (0.02 ppb) were detected in the breathing zone of curing press operators at a Uniroyal plant in Mishawaka, Indiana (NIOSH 1982).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers involved in the production and use of *N*-nitrosodiphenylamine may constitute a group at risk because of the potential for occupational exposure. Persons living near a production facility or a hazardous waste site containing *N*-nitrosodiphenylamine may have a higher risk of exposure to *N*-nitrosodiphenylamine resulting from contact with contaminated air, drinking water, or soil. If microorganisms are found to nitrosate diphenylamine in situ, then workers exposed to this chemical may be at higher risk of *N*-nitrosodiphenylamine exposure. Persons living near facilities producing, or waste sites containing, diphenylamine might also be at increased risk of exposure to *N*-nitrosodiphenylamine via microbial production of the chemical.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of *N*-nitrosodiphenylamine is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of *N*-nitrosodiphenylamine.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce or eliminate the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the

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identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of *N*-nitrosodiphenylamine are sufficiently well defined to allow assessments of the environmental fate of the compound to be made. No additional information is needed.

Production, Import/Export, Use, and Release and Disposal. *N*-Nitrosodiphenylamine is currently produced and used by one manufacturer in the United States (SRI 1990). The general population does not appear to be exposed to any background levels. However, the available data do not permit a confident assessment of the background levels in air, drinking water, or foods. Disposal methods are well documented in the literature (HSDB 1990). More information on current production would be useful in estimating potential exposure to *N*-nitrosodiphenylamine. Further research on the possible production of *N*-nitrosodiphenylamine from diphenylamine by microorganisms would be useful in determining the potential for environmental contamination from this source.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1988, became available in May of 1990. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. *N*-Nitrosodiphenylamine is transported and partitioned in the air, water, and soil. It will sorb to soil and sediment (Swann et al. 1983). It is subject to photolysis in air and biodegradation in water and soil (EPA 1979; Sharma et al. 1986). Additional information regarding hydrolysis and oxidation and the half-lives for these processes would be helpful in determining the persistence of *N*-nitrosodiphenylamine at hazardous waste sites or at production sites where past levels were, or current levels might be, high.

Bioavailability from Environmental Media. Limited available pharmacokinetic data in animals indicate that *N*-nitrosodiphenylamine is absorbed following oral exposure (Appel et al. 1984; Cardy et al. 1979; NCI 1979; Tatsumi et al. 1983). Additional information on the absorption of this compound by these routes would be useful in evaluating the importance of the various routes of exposure to populations living in the vicinity of hazardous waste sites or near a production facility.

Food Chain Bioaccumulation. *N*-Nitrosodiphenylamine is bioconcentrated in aquatic organisms to a limited extent (Barrows et al. 1980). Biomagnification in the aquatic food chain is not a major environmental fate process (Barrows et al. 1980). No data were located regarding bioaccumulation in terrestrial organisms. Since *N*-nitrosodiphenylamine might be found in soil under certain conditions, additional information would be helpful in determining the potential for biomagnification in the terrestrial food chain.

Exposure Levels in Environmental Media. Current monitoring data were not located regarding levels of *N*-nitrosodiphenylamine in air, water, soil, or food. This information would be useful in determining the risk of exposure for populations living near hazardous waste sites or near a production facility. It

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would also aid in determining if contamination due to production of *N*-nitrosodiphenylamine by microorganisms is of environmental concern.

Exposure Levels in Humans. *N*-Nitrosodiphenylamine has been detected in the blood and urine of experimental animals (Pylypiw and Harrington 1981); however, there are no monitoring studies of human populations. Current human studies that monitor *N*-nitrosodiphenylamine in these fluids would be helpful in assessing the potential exposure of individuals who might be exposed through their work or of populations living in the vicinity of a production facility or a hazardous waste site.

Exposure Registries. No exposure registries for *N*-nitrosodiphenylamine were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this substance.

5.7.2 On-going Studies

No on-going studies were located for *N*-nitrosodiphenylamine.